DIPOLE MOMENTS OF SOME SUBSTITUTED BENZENES AND PYRIDINES. PART II META DISUBSTITUTED BENZENES

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ABSTRACT. The dipole moments of *m*-fluorochloro, *m*-fluorobromo and *m*-fluoroiodo benzenes were determined in dilute solution in-benzene. For meta compounds the values agree with those calculated by simple vectorial addition of the group moments, indicating the absence of induced effects.

INTRODUCTION

A survey of the literature on dipole moments shows that not many fluoro compounds have been investigated either in the gaseous state or in the solution state probably because of the difficulty in their preparation. The author could obtain a supply of these compounds through the generosity of Dr. Finger of the Illinois State Geological Survey, to whom he is particularly grateful. For these meta compounds no dipole moment data have been published previously. The author has determined the dipole moment values, making observations in dilute solution in benzene. The values for the ortho compounds have been published by Bergmann *et al.* (1930). Hurdis and Smyth (1942) have determined the dipole moments of para fluorobromo and fluoroiodo benzenes in the vapour phase. The present results would complete the observations on this group of molecules.

EXPERIMENTAL

The experimental arrangement used for measurement of dielectric constants and refractive index of solutions and the method of calculation of dipole moments from the experimental quantities and from the group moments, have been described previously by the author (Murty, 1957). The group moments and polarisabilities used for calculating the dipole moments using Smallwood and Herzfeld's method, are given below:

Group	Moment	Polarisability $\alpha \times 10^{24}$c.c.
F	1.45D	0.57
Cl	1.55	2.51
Br	1.50	3.63
I	1.25	5.46

RESULTS AND DISCUSSION

The experimental results are shown in Tables I, II, and III and consolidated in Table IV together with the calculated values. In Table V are given the observed and calculated values for all these fluoro compounds.

Table V shows that for the meta compounds the simple vectorial moment is in fair agreement with the observed values, whereas for the ortho compounds the agreement is not good—this fact shows that the ortho effects are appreciable for the halogen substituents, although a definite variation with size and polarisability of the substituent group is not noticeable. When the moments are calculated by the Smallwood and Herzfeld method, a much closer agreement is observed for the ortho compounds also. This may further indicate that the ortho effects could be accounted for mostly by mutual inductive effects, the effect due to steric repulsion being negligible.

TABLE I

m-Fluorochloro benzene

W	ε_{12}	$\Delta\varepsilon$	$\Delta\varepsilon/W$	$n^2{}_{12}$	$n^2{}_{12}$	Δn^2	$\Delta n^2/W$
0.01581	2.2960	0.0320	2.023	1.49348	2.23049	0.00017	0.011
0.02189	2.3074	0.0434	1.983	1.49347	2.23044	0.00021	0.010
0.04384	2.3477	0.0837	1.908	1.49347	2 23044	0.00021	0.005
0.06061	2.3776	0.1136	1.875	1.49343	2.23032	0.00033	0.005
0.07630	2.4047	0.1407	1.844	1.49340	2.23024	0.00041	0.005

$P_d = 50.0$ c.c. $\mu = 1.52$ D.

TABLE II

m-Fluorobromo benzene

W	ε_{12}	$\Delta\varepsilon$	$\Delta\varepsilon/W$	n_{12}	$n^2{}_{12}$	Δn^2	$\Delta n^2/W$
0.01311	2.2818	0.0178	1.361	1.49421	2.23269	0.00204	0.156
0.02116	2.2925	0.0285	1.347	1.49471	2.23417	0.00352	0.116
0.03365	2.3103	0.0463	1.377	1.49479	2.23439	0.00374	0.111
0.04832	2.3313	0.0673	1.393	1.49498	2.23497	0.00432	0.089
0.06184	2.3493	0.0853	1.380	1.49493	2.23482	0.00417	0.067
0.08718	2.3843	0.1203	1.380	1.49527	2.23583	0.00518	0.059

$P_d = 39.4$ c.c. 1.40 D.

TABLE III

m-Fluoroiodo benzene

W	ε_{12}	$\Delta\varepsilon$	$\Delta\varepsilon/W$	n_{12}	n^2_{12}	Δn^2	$\Delta n^2/W$
0.03779	2.3058	0.0418	1.105	1.49591	2.23775	0.00711	0.188
0.04930	2.3184	0.0544	1.104	1.49655	2.23965	0.00900	0.183
0.06034	2.3300	0.0660	1.094	1.49697	2.24093	0.01028	0.170
0 07698	2.3473	0.0833	1 082	1.49770	2.24311	0.01246	0.162
0 10420	2.3782	0.1142	1.096	1.49879	2.24637	0.01572	0.151
0.12880	2.4027	0.1387	1.076	1.49985	2.24955	0.01890	0.147

$P_d = 38.3$ c.c. $\mu = 1.38$ D.

TABLE IV

Molecule	Calculated Vector	Calculated S and H	Observed
m–Fluorochloro benzene	1.50	1.45	1.52 D
m–Fluorobromo benzene	1.48	1 42	1.40
m–Fluoroiodo benzene	1.36	1 31	1.38

TABLE V

Molecule	Calculated Vector	Calculated S and H	Observed
o–Fluorochlorobenzene	2.60	2.43	2.38 D
m– ,,	1.50	1.45	1.52
p– ,,	0.10	0.08	0.95*
o–Fluorobromobenzene	2.56	2 36	2.27
m– ,,	1.48	1.42	1.40
p– ,,	0.05	0.05	0.50
o–Fluoroiodobenzene	2.34	2.10	2.00
m– ,,	1.36	1.31	1.38
p– ,,	0.20	0.26	0.90

* Value determined by the author for the pure liquid.

For para compounds there are large differences between the calculated and observed values. The values calculated by taking inductive effects are not very different from those calculated by simple vectorial method. The calculated values show that the moments of these para compounds should be roughly zero.

The large values observed may represent the contributions by atomic polarisations or resonance effect; the possible presence of small amounts of ortho compounds as impurities cannot also be ruled out.

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